5. SOIL ALGORITHMS

In this chapter the algorithms for the transport and transformation of chemical species within and among soil compartments and between the soil compartments and the lower atmosphere and between the soil compartment and surface water are presented. The text box on the next page and continued on the following pages provides a quick summary of the algorithms developed in this chapter and provides a definition of all parameters used.

5.1 INTRODUCTION

Two of the primary processes in subsurface soil are exchange by diffusion and advection. These are key components of the overall rate constant. The transport occurs both in the gas and liquid phase for organic chemicals. The predominant transport mechanism in the aqueous phase is advection, and that in the gas phase is diffusion. The advective transport of contaminants in the liquid or gas phase is dependent on the velocity of that phase. In this application, the total contaminant mass is estimated for each soil compartment. Important physicochemical properties include solubility, molecular weight, vapor pressure, and diffusion coefficients in air and water. The important landscape properties include temperatures of air, rainfall rates, soil properties (bulk density, porosity), and depth of each soil compartment.

There are three advective processes considered in the prototype that can potentially transport a chemical from a soil domain to surface water: erosion of surface soil, runoff from surface soil, and recharge from ground water. Erosion applies to the solid phase, while runoff and recharge applies to the dissolved phase.

5.2 SOIL COMPARTMENTS AND TRANSPORT PROCESSES

In the TRIM.FaTE model, soil is modeled as three distinct compartment types — surface soil, rooting-zone soil, and vadose-zone soil above the saturated zone. In TRIM.FaTE these three regions can be sub-divided into one or more compartments for the purpose of assessing mass transfer. Among these compartment types there are two kinds of transport considered — diffusion and advection. In addition, the uppermost surface soil compartment exchanges mass with the lowest compartment of the atmosphere by a combination of diffusion and advection processes.

5.3 TRANSFORMATIONS IN SOIL COMPARTMENTS

The transformation of contaminants in soil layers can have a profound effect on their potential for persistence. Chemical transformations, which may occur as a result of biotic or abiotic processes, can significantly reduce the concentration of a substance. For all chemical reactions, knowledge of a compound's half-life for any given transformation process provides a very useful index of persistence in environmental media. Because these processes determine the persistence and form of a chemical in the environment, they also determine the amount and type of substance to which a human or ecological receptor could be exposed. In the TRIM.FaTE soil

Summary of Transport Algorithms Developed in this Chapter

Lowest air compartment to upper surface soil compartment:

$$T_{a \to i} = \left[\frac{U_{air} \times Area_i \times Z_{air}}{V_a \times Z_a} \right] + \left\{ V_d [PC / \rho_p][Z_{ap} / Z_a] + rain[Z_{water} / Z_a] \right\} \times [Area_i / V_a]$$

First soil compartment to lowest air compartment:

$$T_{i \to a} = \left[\frac{U_{air} \gamma_i}{[1 - \exp(-\gamma_i d_i)]} \right] Z_{air} / Z_i + [Respnd / \rho_{si}][Z_{si} / Z_i] \times [Area_i / V_a]$$

Downward flow from soil compartment i to soil compartment j:

$$T_{i \to j} = \frac{Y_{ij}}{d_i Z_i} + \frac{ve_i \gamma_i}{\left(e^{+\gamma_i d_i} - 1 \right)}$$

Upward flow from soil compartment j to soil compartment i:

$$T_{j \to i} = \frac{Y_{ij}}{d_j Z_j}$$

Horizontal runoff from compartment i to compartment j:

$$T_{i \to j}(runoff) = Runoff \times f_{run}(ij) \times Z_i(rain) / (Z_i d_i *)$$

where

U_{air}	=	mass transfer coefficient on the air side of the air/soil boundary, m/d (It is typical to represent the mass transfer coefficient in air as ratio of the diffusion coefficient in air, D_{air}, divided by the turbulent boundary compartment thickness, δ_{air}. For many compounds, D_{air} is on the order of 0.4 m/d and δ_{air} is on the order of 0.0005 m, so that U_{air} is on the order of 800 m/d.)
$Area_i$	=	horizontal area of the soil compartment, m^2 (This is the area assumed to be shared between the top soil compartment and the atmosphere and between any two adjacent soil compartments.)
V_a	=	volume of the air compartment, m^3.
Z_{air}	=	fugacity capacity of pure air, = 1/RT, mol/(m^3-Pa).
Z_a	=	total fugacity capacity of the air compartment (includes gas and particle phase of the atmosphere), mol/(m^3-Pa).
Z_{ap}	=	fugacity capacity of air particles, mol/(m^3-Pa).

Summary of Transport Algorithms Developed in this Chapter (cont.)

V_d	=	air-to-soil deposition ratio, mol/m^2/d per mol/m^3 (includes only deposition that is not intercepted by plants, and is calculated as the total deposition velocity times one minus the plant interception fraction), ~ 400 m/d.
PC	=	particulate matter concentration in air, ~ 6.0 x 10^{-8} kg/m^3.
ρ_p	=	density of particulate matter in air, ~ 2600 kg/m^3 (Wilson and Spengler 1996).
$rain$	=	rate of rainfall, m/d.
Z_{water}	=	fugacity capacity of the moving phase, water, mol/(m^3-Pa).
$Area_i$	=	area of contact between the surface soil compartment and the lowest air compartment, m^2.
Z_i	=	total fugacity capacity of soil compartment i, mol/(m^3-Pa).
Z_{si}	=	fugacity capacity of soil compartment i, mol/(m^3-Pa).
d_i	=	thickness of soil compartment i, m.
Y_{ij}	=	fugacity-capacity adjusted mass transfer coefficient between compartments i and j, mol/(m^2-Pa-day), and is given by:

$$Y_{ij} = \frac{Z_i De_i \gamma_i + Z_j De_j \gamma_j}{2\left[\dfrac{\left(e^{+\gamma_i d_i} - 1\right)}{\gamma_i d_i} - \dfrac{\left(1 - e^{-\gamma_j d_j}\right)}{\gamma_j d_j}\right]}$$

De_i	=	effective diffusion coefficient in soil compartment i, m^2/d.
ve_i	=	effective advection velocity of a chemical in the soil compartment i, m/d, and equal to the rate of soil-solution movement, v_i, multiplied by the fugacity capacity of soil compartment i; $ve_i = v_i Z_{water}/Z_i$.
v_i	=	average velocity of the moving phase (assumed to be water) in the soil compartment i, m^{-1}.
γ_i	=	gradient of soil concentration change in soil compartment i, m^{-1}. Obtained from the inverse of the normalized or characteristic depth X*, that is $\gamma_i = 1/X^*$.

X* is obtained as follows:

      If $\lambda_i > 0$ then X* = Minimum (DX$_1$, DX$_2$)
            Otherwise, if $\lambda_i = 0$, then X* = DX$_2$.

DX$_1$ is the Damkoehler distance (the distance at which the soil concentration falls by 1/e based on the competition among diffusion, advection, and reaction) and is given by:

$$DX_1 = \frac{ve_i + \sqrt{ve_i + 4De_i}}{2\lambda_i}$$

DX$_2$ is the depth that establishes the concentration gradient in soil in the absence of any reaction or transformation processes. It is obtained as follows:

      If $ve_i > 0$, then DX$_2$ = Minimum (4De$_i$/ve$_i$, DX$_{sat}$)
      If $ve_i = 0$, then DX$_2$ = Minimum (2d$_i$, $\sqrt{\pi}$, DX$_{sat}$)

Summary of Transport Algorithms Developed in this Chapter (cont.)

λ_i	=	removal rate constant for a chemical in soil compartment, based on chemical transformation, day^{-1}.
Respnd	=	rate at which dust is resuspended from the soil surface, kg/m^2/d.
ρ_{si}	=	density of dust particles, kg/m^3.
α	=	volume fraction of the soil compartment that is gas, unitless.
β	=	volume fraction of the soil compartment that is water, unitless.
ϕ	=	total void fraction in soil compartment, unitless, $\phi = \alpha + \beta$.
Rh	=	hydraulic radius of water flowing over surface soil during a rain event, assumed to be 0.005 m.
d_i	=	depth of surface soil compartment during periods of no rain, m.
d_i^*	=	effective depth of saturated surface soil during a rain event, m, $d_i^* = Rh + d_i$
Runoff	=	flux of water transported away from surface soil compartment *i*, m^3/m^2-day.
$f_{run}(ij)$	=	fraction of water that runs off of surface soil compartment *i* that s transported to compartment *j*, unitless.

layers, all transformation processes are modeled as first-order processes; that is, linear with inventory (*i.e.*, the quantity of chemical substances contained in a compartment). The rate of mass removal in a first-order transformation is calculated as the product of the total inventory and the transformation rate constant. The transformation rate constant is the inverse of the residence time with respect to that reaction.

5.4   VERTICAL TRANSPORT ALGORITHMS

The transfer factors in the subsurface are a function of the advective flux (gas phase plus liquid phase) and the diffusive flux (gas phase plus liquid phase). In the sections below, upward and downward transfer factors are developed for the soil compartments. No provisions are made for preferential flow regions in the vadose zone that could lead to higher concentrations in the ground water because in most cases, the proportion of exposure from ground water is minimal for air pollutants.

5.4.1   THEORETICAL BASIS FOR THE TRANSPORT ALGORITHMS

The algorithms below are developed by assuming that chemical concentration in each compartment decreases exponentially with depth in that compartment. This type of concentration gradient has been demonstrated as the correct analytical solution of the one-dimensional, convective-dispersive, solute-transport equation in a vertical layer with a steady-state concentration maintained at its upper surface (ARS 1982). With the assumption of exponentially decreasing vertical concentration for each soil compartment, *i*, the variation in concentration with depth in that compartment is given by:

$$C_i(x) = C_i(0)\exp(-\gamma_i x) \tag{5-1}$$

where:

x = distance into the soil compartment measured from the top of the soil column (m);

$C_i(0)$ = peak chemical concentration in soil compartment *i* (mol/m^3), which is related to the total inventory N_i (moles) in this soil compartment (this relationship is provided below);

γ_i = the gradient of soil concentration change in soil compartment *i* (m^{-1}), and is obtained from the inverse of the normalized or characteristic depth X^*, that is $\gamma_i = 1/X^*$.

X^* is obtained as follows:

If $\lambda_i > 0$ then $X^* = $ Minimum (DX_1, DX_2)
   Otherwise, if $\lambda_i = 0$, then $X^* = DX_2$. (5-2)

DX_1 is the Damkoehler distance (the distance at which the soil concentration falls by 1/e based on the competition among diffusion, advection, and reaction) in units of meters and is given by:

$$DX_1 = \frac{ve_i + \sqrt{ve_i + 4De_i}}{2\lambda_i} \qquad (5\text{-}3)$$

DX_2 is the depth that establishes the concentration gradient in soil in the absence of any reaction or transformation processes, in units of meters. It is obtained as follows:

If $ve_i > 0$, then $DX_2 = $ Minimum $(4De_i/ve_i, DX_{sat})$
If $ve_i = 0$, then $DX_2 = $ Minimum $(2d_i, \sqrt{(\pi)}, DX_{sat})$ (5-4)

ve_i =   the effective advection velocity of a chemical in the soil compartment, i (m/day), and equal to the rate of soil-solution movement, v_i, multiplied by the fugacity capacity of the moving phase and divided by the fugacity capacity of soil compartment i;

$$ve_i = v_i \, Z_{water}/Z_i \qquad [5\text{-}5]$$

v_i =   the average velocity of the moving liquid phase (assumed to be water) in the soil column i (m/day);
DX_{sat} =   depth to saturation in the soil column (m);
d_i =   the thickness of soil compartment i (m);
Z_{water} =   the fugacity capacity of the moving phase, water (mol/[m³-Pa]);
Z_i =   the total fugacity capacity of soil compartment i (mol/[m³-Pa]);
λ_i =   removal rate constant for a chemical in soil compartment i, based on chemical transformation (day⁻¹); and
De_i =   effective diffusion coefficient in soil compartment i (m²/d), and is derived below.

Compartments such as soils and sediments are neither homogeneous nor single phase. When air and water occupy the tortuous pathways between stationary particles in a porous medium such as a soil or sediment, Millington and Quirk (1961) have shown that the effective diffusivity, D_{eff}, of a chemical in each fluid of the mixture is given by:

$$D_{eff} = (\omega^{10/3} / \phi^2) D_{pure} \qquad (5\text{-}6)$$

where ω (α for gas fraction and β for water fraction) is the volume fraction occupied by this fluid, ϕ is the total void fraction in the medium (the volume occupied by all fluids) , and D_{pure} is the diffusion coefficient of the chemical in the pure fluid. Jury et al. (1983) have shown that the effective tortuous diffusivity in the water and air of a soil compartment, such as the root-zone soil(s), is given by:

$$De_i = \frac{Z_{air}}{Z_i}(\alpha_i^{10/3} / \phi_i^2)D_{air} + \frac{Z_{water}}{Z_i}(\beta_i^{10/3} / \phi_i^2)D_{water} \tag{5-7}$$

where De_i is the effective tortuous, mixed phase diffusion coefficient in the root-zone soil compartment, the Z's are the fugacity capacities derived previously.

5.4.2 RELATIONSHIP BETWEEN INVENTORY, N_i, AND PEAK CONCENTRATION, $C_i(0)$

The assumptions of a peak chemical concentration and an exponential gradient of chemical concentration within a soil compartment makes it possible to define $C_i(0)$ in terms of N_i:

$$N_i = Area_i \int_0^{d_i} C_i(0)\exp(-\gamma_i x)dx \tag{5-8}$$

$$N_i = Area_i[C_i(0) / \gamma_i][1 - \exp(-\gamma_i d_i)] \tag{5-9}$$

where:

N_i	=	compartment inventory (mol)
C_i	=	compartment concentration (mol/m^3)
d_i	=	thickness of soil compartment i (m); and
$Area_i$	=	horizontal area of the soil compartment (m^2).

Rearranging the right term of Equation 5-9 gives:

$$C_i(0) = \frac{N_i\gamma_i}{Area_i[1 - \exp(-\gamma_i d_i)]} \tag{5-10}$$

5.4.3 VERTICAL MASS EXCHANGE BETWEEN AIR AND THE UPPER SURFACE SOIL COMPARTMENT

The algorithm for representing diffusion exchange at the air/soil interface is based on defining the flux from air to soil in terms of the concentration gradient at the point of contact between air and soil.

$$Flux = U_{air}\left[C_{air} - C_i(0)\frac{Z_{air}}{Z_i}\right] \tag{5-11}$$

where:

U_{air} = mass transfer coefficient on the air side of the air/soil boundary (m/d) (It is typical to represent the mass transfer coefficient in air as the ratio of the diffusion coefficient in air, D_{air}, divided by the turbulent boundary compartment thickness, δ_{air}. For many compounds, D_{air} is on the order of 0.4 m/d and δ_{air} is on the order of 0.0005 m, so that U_{air} is on the order of 800 m/d.)

C_{air} = bulk concentration of chemical agent in the lowest compartment of the atmosphere, mol/m³ and given by $C_{air} = N_a Z_{air}/[V_a Z_a]$, where N_a is the inventory (in mol) of the air compartment above the soil, Z_{air} is the fugacity capacity of pure air, V_a is the volume (in m³) of this compartment, and Z_a is the total fugacity capacity of the air compartment (includes gas and particle phase of the atmosphere).

$C_i(0)$ = chemical concentration at the top of the uppermost soil compartment in a vertical set of soil compartments, ml/m³, as given by Equation 5-6. There can be several vertical soil compartment sets in a model run.

Z_{air} = fugacity capacity of pure air, = 1/RT, mol/(m3-Pa).

Making the appropriate substitutions, the net flow of mass between air and soil by diffusion is calculated as:

Net Diffusion Flow ($a \leftrightarrow i$) (mol/day)

$$= Flux \times Area_i = U_{air}\left[\frac{Area_i \times Z_{air}}{V_a \times Z_a}N_a - \frac{\gamma_i}{[1-\exp(-\gamma_i d_i)]}\frac{Z_{air}}{Z_i}N_i\right] \qquad (5\text{-}12)$$

It is important to note that the area used to calculate the flux is $Area_i$, the surface area of the soil compartment i that is shared with the lowest atmosphere compartment. This is not necessarily the surface area of the lowest atmosphere compartment.

For dry and wet deposition of particles from air to soil, the rate of mass flow is given by:

Particle Advection Flow (a→i) (mol/d)

$$= V_d[PC/\rho_p][Area_i/V_a][Z_{ap}/Z_a]N_a \qquad (5\text{-}13)$$

where:

V_d = air-to-soil deposition ratio (includes only deposition that is not intercepted by plants, and is calculated as the total deposition velocity times one minus the plant interception fraction (mol/m²/d per mol/m³) $\sim$ 400 m/d;

PC = particulate matter concentration in air $\sim 6.0 \times 10^{-8}$ kg/m³;

ρ_p = density of the particulate matter in air ~ 2600 kg/m³;

$Area_i$ =   area of contact between the surface soil compartment and the lowest air
            compartment (m^2); and

V_a =   volume of the air compartment (m^3).

For rainfall, the advection flow of chemical from air to the upper surface soil
compartment is given by:

Rain Advection Flow ($a \rightarrow i$) (mol/d)

$$= rain[Z_{water} / Z_a][Area_i / V_a]N_a \qquad (5\text{-}14)$$

where:

Z_{water} =   fugacity capacity of pure water (*i.e.*, no suspended sediments)
Z_a =   fugacity capacity of the air compartment (mol/m^3-Pa)
$rain$ =   the rate of rainfall (m/d).

For re-suspension of dust from the first surface soil compartment to the lower
compartment of the atmosphere, the chemical flow from soil to air is given by:

Advection Flow ($i \rightarrow a$) (mol/d)

$$= [Respnd / \rho_{si}][Z_{si} / Z_i][Area_i / V_a]N_i \qquad (5\text{-}15)$$

where:

$Respnd$ =   rate at which dust is resuspended from the soil surface
            (kg/m^2/d); and

ρ_{si} =   density of the dust particles (kg/m^3).

Combining Equations 5-12 through 5-15 provides the following transfer-rate factors for
the exchange of chemical species between the lowest atmosphere compartment and the surface
soil compartment:

$$T_{a \rightarrow i} = \left[\frac{U_{air} \times Area_i \times Z_{air}}{V_a \times Z_a} \right] + \left\{ V_s \left[\frac{PC}{\rho_p} \right] \left[\frac{Z_{ap}}{Z_a} \right] + rain \left[\frac{Z_{water}}{Z_a} \right] \right\} \times \left[\frac{Area_i}{V_a} \right] \qquad (5\text{-}16)$$

$$T_{i \rightarrow a} = \left[\frac{U_{air} \gamma_i}{[1 - \exp(-\gamma_i d_i)]} \right] \left[\frac{Z_{air}}{Z_s} \right] + \left[\frac{Respnd}{\rho_{si}} \right] \left[\frac{Z_{si}}{Z_i} \right] \times \left[\frac{Area_i}{V_a} \right] \qquad (5\text{-}17)$$

5.4.4 VERTICAL MASS EXCHANGE BETWEEN TWO VERTICALLY ADJACENT SOIL COMPARTMENTS

The vertical exchange of a chemical substance between two vertically adjacent soil compartments occurs through advection and diffusion. Only the net advection in the downward direction is considered due to long-term infiltration of rainwater. According to Equation 5-1, the concentration in each soil compartment i is given by:

$$C_i(x) = C_i(0)\exp(-\gamma_i x)$$ (same as 5-1 above)

where x is measured from the top of the soil compartment i. Thus, the diffusion flow at the lower boundary of soil compartment i to compartment j is given by:

$$diffusion\ flow = -Area \times De_i \frac{dC}{dx}\bigg|_{d_i} = Area \times De_i \times C_i(0) \times \gamma_i e^{-\gamma_i d_i}$$ (5-18a)

where:

De_i = effective diffusion coefficient in soil compartment i, m2/d
d_i = the thickness of soil compartment i, m;

Conservation of mass requires that flow specified by equation 5-18 out of compartment i must equal the flow into compartment j at the upper boundary of compartment j, that is:

$$diffusion\ flow = -Area \times De_j \frac{dC}{dx}\bigg|_0 = Area \times De_j \times C_j(0) \times \gamma_j$$ (5-18b)

Combining equations 5-18a and 5-18b gives:

$$diffusion\ flow = Area \times \frac{\left[De_i \times C_i(0) \times \gamma_i e^{-\gamma_i d_i} + De_j \times C_j(0) \times \gamma_j\right]}{2}$$ (5-19)

$C_i(0)$ is found from the condition:

$$N_i = Area \int_0^{d_i} C_i(0)e^{-\gamma_i x}dx = Area \times \frac{C_i(0)}{\gamma_i} \times \left(1 - e^{-\gamma_i d_i}\right)$$ (5-20)

Rearranging gives:

$$C_i(0) = \frac{N_i \gamma_i}{Area \times \left(1 - e^{-\gamma_i d_i}\right)}$$ (5-21)

In order to conserve concentration equilibrium at the boundary between two soil compartments, the following condition must hold:

$$C_j(0) = \frac{Z_j}{Z_i} C_i(0) e^{-\gamma_i d_i} = \frac{Z_j}{Z_i} \times \frac{N_i \gamma_i \times e^{-\gamma_i d_i}}{Area \times \left(1 - e^{-\gamma_i d_i}\right)}$$

(5-22)

Substituting equations 5-21 and 5-22 into equation 5-19 gives

$$diffusion\ flow = \frac{N_i \gamma_i}{Z_i \left(e^{+\gamma_i d_i} - 1\right)} \times \left(\frac{De_i \gamma_i Z_i + De_j \gamma_j Z_j}{2} \right)$$

(5-23)

Then in order to express mass transfer between two compartments, the diffusion flow is represented in the following form:

$$diffusion\ flow = Area \times Y_{ij} \left(\frac{N_i}{Z_i V_i} - \frac{N_j}{Z_j V_j} \right)$$

(5-24)

where:

Y_{ij} =   fugacity-capacity adjusted mass transfer coefficient between compartments i and j, mol/(m²-Pa-day).

N_j, the total inventory in compartment j is given by:

$$N_j = Area \int_0^{d_j} C_j(0) e^{-\gamma_j x} dx = Area \times \frac{C_j(0)}{\gamma_j} \times \left(1 - e^{-\gamma_j d_j}\right)$$

(5-25)

Substituting equation 5-23 in equation 5-25 gives:

$$N_j = \frac{Z_j N_i \times \gamma_i \times \left(1 - e^{-\gamma_j d_j}\right)}{Z_i \times \gamma_j \times \left(e^{+\gamma_i d_i} - 1\right)}$$

(5-26)

An expression for Y_{ij} is obtained by substituting equation 5-26 for N_j in equation 5-24 and then setting equation 5-24 equal to equation 5-23:

$$\frac{N_i \gamma_i}{Z_i \left(e^{+\gamma_i d_i} - 1\right)} \left(\frac{De_i \gamma_i Z_i + De_j \gamma_j Z_j}{2} \right) = Y_{ij} \frac{N_i}{Z_i} \left(\frac{1}{d_i} - \frac{\gamma_i \times \left(1 - e^{-\gamma_j d_j}\right)}{d_j \times \gamma_j \times \left(e^{+\gamma_i d_i} - 1\right)} \right)$$

(5-27)

Rearranging gives:

$$Y_{ij} = \frac{Z_i De_i \gamma_i + Z_j De_j \gamma_j}{2\left[\dfrac{\left(e^{+\gamma_i d_i} - 1\right)}{\gamma_i d_i} - \dfrac{\left(1 - e^{-\gamma_j d_j}\right)}{\gamma_j d_j}\right]} \tag{5-28}$$

The definition of Y_{ij} in equation 5-28 completes the definition of all terms in equation 5-24.

The advection flux from soil compartment i to j at the lower end, d_i, of compartment i is given by:

$$advection\ flow(i\ to\ j) = Area \times ve_i \times C_i(0)\exp(-\gamma_i d_i) \tag{5-29}$$

where:

ve_i = the effective advection velocity of a chemical in the soil compartment, i; m/d, and equal to the rate of soil-solution movement, v_i, multiplied by the fugacity capacity of the moving phase and divided by the fugacity capacity of soil compartment i;

$$ve_i = v_i Z_{water} \Big/ Z_i$$

v_i = the average velocity of the moving phase (assumed to be water) in the soil compartment, i; m^{-1}.

Substituting Equation 5-21 for $C_i(0)$ in Equation 5-29 gives:

$$advection\ flow(i\ to\ j) = \frac{N_i \gamma_i ve_i}{\left(e^{+\gamma_i d_i} - 1\right)} \tag{5-30}$$

Combining Equations 5-24 and 5-30 and multiplying by $Area_i$, gives the flow from i to j as:

net total flow (mol/d) (i to j) = [*net diffusion flow + advection flow*] (i to j)

$$= Y_{ij}\left(\frac{N_i}{Z_i d_i} - \frac{N_j}{Z_j d_j}\right) + \frac{N_i \gamma_i ve_i}{\left(e^{+\gamma_i d_i} - 1\right)} = T_{i \to j} N_i - T_{j \to i} N_j \tag{5-31}$$

From this equation, we can derive terms for $T_{i \to j}$ and $T_{j \to i}$:

$$T_{i \to j} = \frac{Y_{ij}}{d_i Z_i} + \frac{v e_i \gamma_i}{\left(e^{+\gamma_i d_i} - 1\right)} \tag{5-32}$$

$$T_{j \to i} = \frac{Y_{ij}}{d_j Z_j} \tag{5-33}$$

5.5 STORM WATER RUNOFF PROCESSES

Horizontal transport processes included in TRIM.FaTE include solution runoff and erosion.

5.5.1 AQUEOUS PHASE TRANSPORT PROCESSES

During a rainfall event, some of the water travels laterally across the soil as runoff. As the water travels over the soil, the concentration of the water approaches that of the soil pore water beneath it. Although the water flowing over the soil does not necessarily reach equilibrium instantaneously, some researchers use an approximation that runoff is in equilibrium with the soil pore water (Wallach et al. 1989). Currently in TRIM.FaTE, a steady-state relationship between the runoff water and the pore water is used. Runoff water is considered a phase of surface soil compartment at each spatial location. A mass-balance approach is used to determine the concentration in run-off water that moves from one soil compartment to a horizontally adjacent compartment.

Runoff transport is assumed to carry chemical from the surface soil compartment of one land unit to the next. During a rain event the surface soil compartment is assumed to be saturated with rain water and this water is assumed to be in equilibrium with the soil solids on the surface. It should be recognized that at times (*e.g.*, short rain events, during very dry periods of the year) the soil will not necessarily be fully saturated with rain water. However, the assumption of saturation by rain is not expected to have a large impact on results for events when the soil is not saturated. Moreover, a lack of information on the extent to which soil is saturated during rain makes this a convenient starting point. The assumption of that chemical equilibrium has more uncertainty and needs further research. During periods of no rain, the fugacity capacity of the surface soil compartment is given by:

$$Z_i = \alpha Z_{air} + \beta Z_{water} + (1 - \phi) Z_{si} \tag{5-34}$$

During periods of rain, the fugacity capacity of the surface soil compartment is given by:

$$Z_i(rain) = [(Rh + \phi d_i) Z_{water} + (1 - \phi d_i) Z_{si}] / d_i * \tag{5-35}$$

where:

Z_{water} = fugacity capacity of pure water (*i.e.*, no suspended sediments)

Z_{si} = fugacity capacity of the solids (or solid phase) in the ith soil layer (mol/m³-Pa)

α = volume fraction of the surface soil that is gas;

β = volume fraction of soil that is water;

ϕ = total void fraction in surface *soil*, $\phi = \alpha + \beta$;

Rh = hydraulic radius of the water flowing over the surface soil during a rain event, assumed to be 0.005 m;

d_i = depth of the surface soil compartment during periods of no rain (m); and

d_i* = effective depth of the saturated surface soil during a rain event (m), $d_i* = Rh + d_i$.

The hydraulic radius, Rh, for flow of water on top of the soil surface is site specific and depends on the hydraulic gradient (slope of the flow), the rainfall rate, and the recharge rate. It is considered an uncertain variable, but is assigned a default value of 0.005 m. A hydraulic balance is needed to determine the flow of the water and the depth of the runoff stream. From the Geographic Information System (GIS) data, the runoff is estimated.

During a rain event, the horizontal flow of chemical from surface soil compartment *i* to adjacent compartment *j* is given by:

$$Runoff\ flow(i \to j) = Runoff \times f_{run}(i \to j) \times Z_i(rain)/Z_i/d_i* \qquad (5\text{-}36)$$

where:

Runoff = flux of water that is transported away from surface soil compartment *i* (m³/m²-day); and

$f_{run}(i{\to}j)$ = fraction of water that runs off of surface soil compartment *i* that is transported to compartment *j* (unitless).

From Equation 5-36, the expression for $T_{i \to j}(runoff)$ can be obtained:

$$T_{i \to j}(runoff) = Runoff \times f_{run}(i \to j) \times Z_i(rain)/(Z_i d_i*) \qquad (5\text{-}37)$$

5.5.2 SOLID PHASE TRANSPORT PROCESSES

The algorithm for erosion runoff is based on knowledge of the erosion factor for the region being modeled. Similar to solution runoff, erosion is also applied only to the surface soil layer. Although erosion is most likely to occur during rain events, erosion can be modeled as a continuous event. The flow of chemical (mol/d) from one surface soil compartment to another by erosion is represented by the following expression:

$$Erosion\ flow\ (i{\to}j) = erosion \times f_{ero}\ (i{\to}j) \times Z_{si}/Z_i \times N_i/(\rho_{si} d_i) \qquad (5\text{-}38)$$

where:

erosion	=	erosion factor (kg of soil solids eroded per day per m^2);
$f_{ero}(i{\rightarrow}j)$	=	fraction of soil eroded from surface soil compartment i that is transported to compartment j (unitless);
Z_{si}	=	fugacity capacity of the soil particles in soil compartment i (mol/[m^3-Pa]);
ρ_{si}	=	density of the soil particles, $\sim$ 2600 kg/m^3.

From Equation 5-36, the expression for $T_{i{\rightarrow}j}(erosion)$ can be obtained:

$$T_{i{\text{->}}j}(erosion) = erosion \times f_{ero}(i{\rightarrow}j) \times Z_{si} / (Z_i\,\rho_{si}\,d_i) \qquad\qquad [5\text{-}39]$$

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